Unzipping of Multiwalled Carbon Nanotubes

Dissertation submitted in partial fulfilment of the requirements for the degree of

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Branch: PHYSICS

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ABSTRACT

Carbon nanotubes (CNTs) were first brought to the attention of greater scientific community by S. Ljima of Japan in 1991. CNTs are members of the fullerene (C_{60}) structural family. Their name is derived from their long and hollow structures with the walls formed by one atom thick sheets of carbon, called graphene. This graphene is a two-dimensional (2D) material exhibits exceptionally high crystal and electronic quality. Despite its short history it has already revealed a cornucopia of new physics and potential applications due to high charge carrier mobility, exceptional mechanical and electrical properties. However the low cost, good quality graphene synthesis is a big challenge to the science society. In this report I will describe the fabrication of graphene nanoribbons from carbon nanotubes (CNT) treated with potassium permanganate in a concentrated sulphuric acid solution reported by Dmitry V. Kosynkin and Amanda L. Higginboth in nature paper Vol. 458| 16 April 2009| doi:10.1038/nature07872.

Keywords – *CNT, Graphene, Unzip, Oxidation*

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CHAPTER 1

INTRODUCTION

1.1 Graphene family and Carbon Nano Tube (CNT):

One major breakthrough in the field of nanotechnology happened with the discovery of the third allotropic form of carbon, next to '*diamond'* and '*graphite'*; the '*fullerenes'*. [1] Fullerenes are the hollow molecules entirely composed of carbon. Carbon nanotubes (CNT) are members of the fullerene structural family. Their name is derived from their long and hollow structures with the walls formed by one atom thick sheets of carbon, called *graphene*. CNT's are fullerenes carbon cages, in which sp^2 carbons are directly bonded to three neighbors in an arrangement of five-six membered rings. [2]

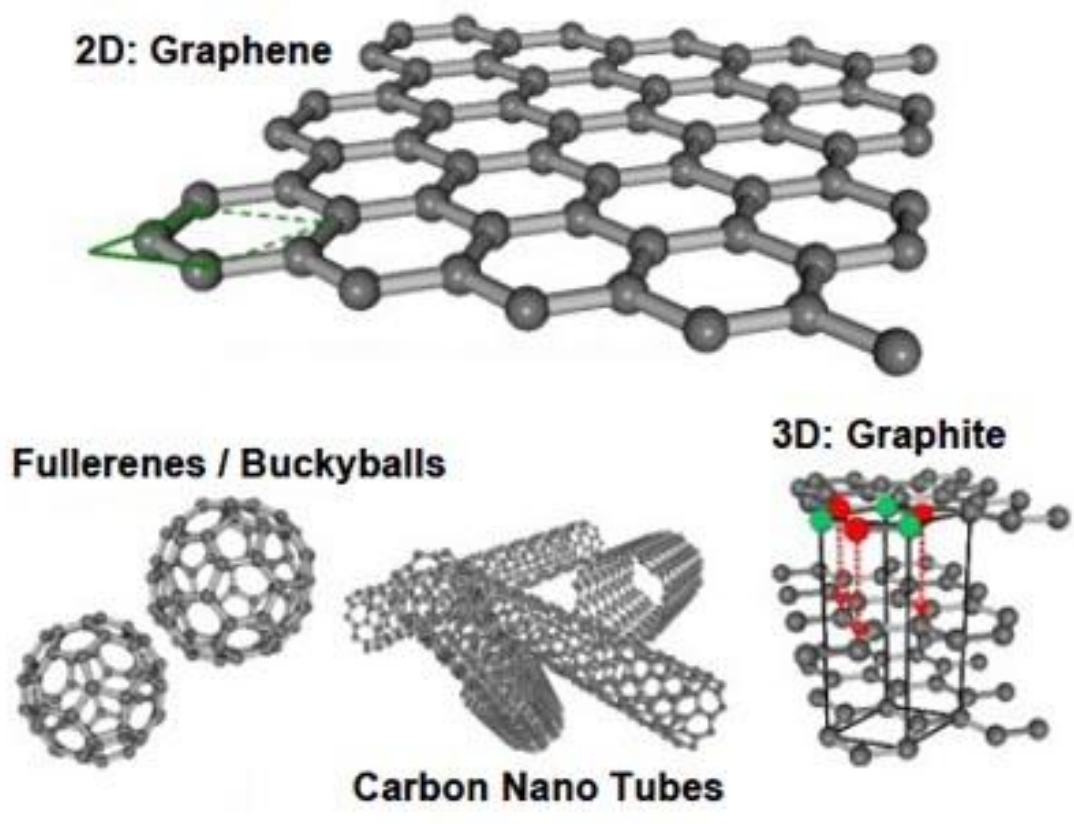

Fig. 1.1 – Graphene, Fullerenes & CNT

1.2 Types of CNT

The structure of CNT consists of enrolled graphitic sheet, in a word; it can be classified into two ways depending on its structure, single walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). The two forms of CNTs show different electrical and mechanical characteristics. [3]

CNTs were first discovered in 1991 by the scientist Sumio Iijima (Japan). The outer diameters of MWCNT have range from 1 to 50 nm while the inner diameter is usually of several nanometers. (3 & 2.2 nm by ***Sumio Lijima***; 1991) [4]

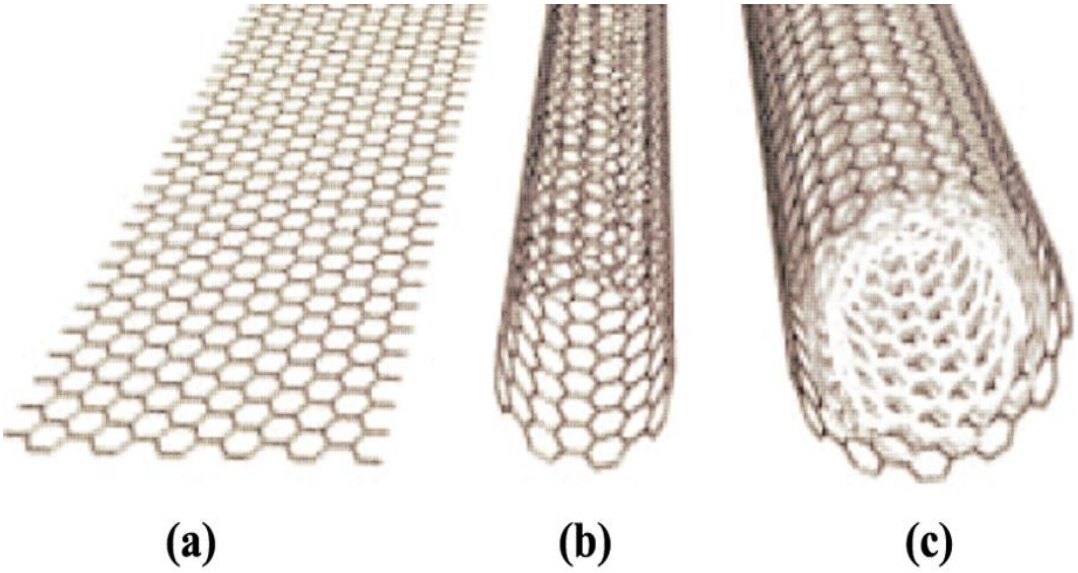

Fig. 1.2 – (a) Graphene, (b) SWCNT, (c) MWCNT

These graphene sheets are rolled at specific and discrete (chiral) angles, and these combination of the rolling angles and radius decides the nanotube properties. They can be semiconducting or metallic depending on their structure. [5] The way the graphene sheet wraps can be represented by a pair of indices (n, m) called the chiral vector. The relationship between n and m defines three categories of CNT.

(i) Arm chair (n = m and chiral angle equal to 30°)

(ii) Zigzag (n = 0 or m = 0 and chiral angle equal to 0°)

(iii) Chiral (other values of n and m and chiral angles lie between 0 and 30°) [4].

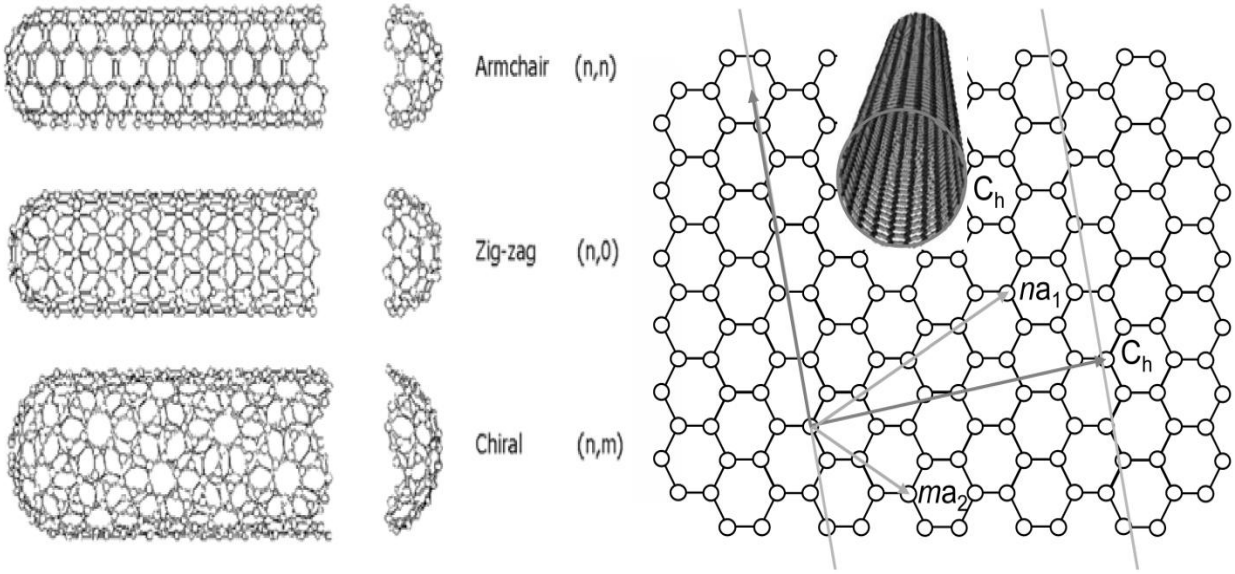

Fig. 1.3 – Three types of CNTs
(Armchair, Zig-zag, Chiral)

1.3 Carbon bonds in CNT

Graphene can be considered to be made of benzene rings joined together and stripped of their hydrogen atoms. Isolated single carbon atom has four valence electrons. In graphene three atomic orbital are hybridized into a trigonal planar structure. So it forms three covalent σ bonds (sp^2-hybridization) with other three carbon atoms. Those strong bonds are responsible for the robustness of graphene. The remaining fourth valence electrons form covalent π- bond with neighboring carbon atoms and those are responsible for the electronic properties. [6]

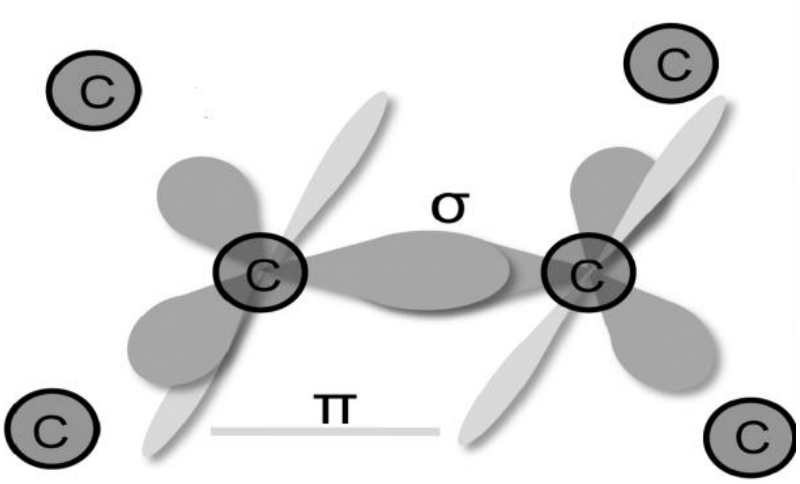

Fig. 1.4 - Schematic image of the sp2-hybridization [6]
(3 sp^2-orbitals and 1 p_z-orbital)

1.4 Dominances of Graphene:

1. Carbon-carbon bonds are one of the strongest bonds in nature. Graphenes are composed of perfect arrangement of these bonds. So it shows extremely high Young's modulus 1000 GPa (steel – 200Gpa). It may replace steel in the future and can be use in construction purposes like using nanocomposites bridges and dams [7].
2. Its light and low mass property helping aerospace industries to build aircrafts and satellites.
3. Graphene has high conductivity (resistance is 10^{-6} Ω/cm at room temperature) and dissipates heat quickly. Hence can be applied in fabrication of electrical devices as interconnects transistors, CMOS industry, and nanaowires [5, 7].
4. Their unique properties of graphene could possibly be used to make faster and smaller computers and tiny sensors that powerful enough to detect a single molecule.

1.5 Methods of preparation of Graphene

There are various methods to prepare mwcnt; such as

a. Chemical vapour deposition (CVD) [15]
b. Laser abalation
c. Arc discharge
d. Electrochemical method
e. Pulsed laser vaporization (PLV)
f. Plasma enhanced chemical vapour deposition (PECVD)
g. Aerosol method
h. Solution methods
i. Solvothermal method etc. [8]

1.6 Why unzipping:

However, graphene have not yet made inroads into the electronics or other sectors, because they are difficult to make defined pure structures in large quantities. At present, they are produced in batches, with only a handful of graphenes in each batch possessing the desired characteristics. This approach works well for laboratory research, but is too inefficient for commercial applications. Unzipping MWCNT is an efficient way to produce graphene.

Graphene show promising applications in science and technology due to its exotic properties. Hence focus is on to prepare good quality of graphene by adopting various methods. Graphene produced by all above methods are irregular in size. Future nanoelectronic applications of graphene s are hampered by irregular size that is due to its edge scattering . This mechanism changes the physical properties of graphene.

The regular size 2D graphene nanosheets would be better in order to avoid the edge effect and could be used in its full potential.

The the regular size graphene sheets could be obtained by unzipping the CNTs.

1.7 The unzipping process:

Multiwalled nanotubes (MWVNT) consist of multiple rolled layers (concentric tubes) of graphene. Unzipping is a technique that cut multiwalled carbon nanotubes (MWCNT) crossway to form graphene. (Fig. 1.4) [9]

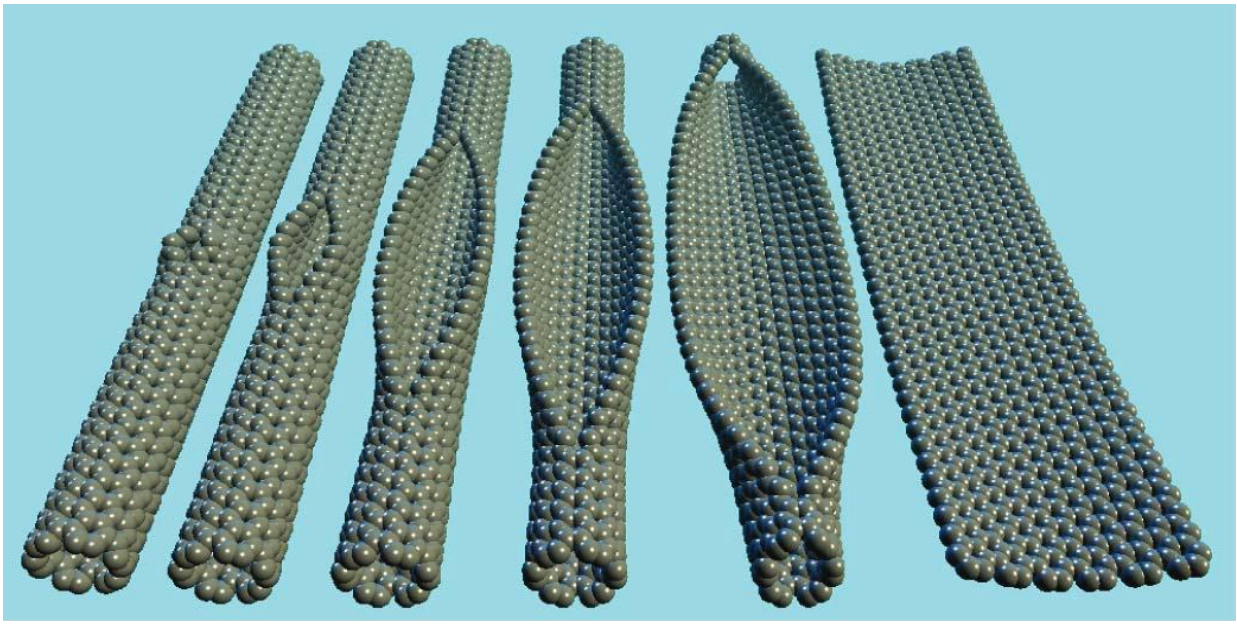

Fig. 1.5 - The Unzipping Process

1.8 Different types of unzipping:

1. *"**Fabrication methods**"* for Graphene based on longitudinally cutting CNTs have also been reported recently. Jiao et al.2 obtained narrower semiconductor ribbons by embedding multiwalled carbon nanotubes in a polymer matrix and then attacking the surface with argon plasma etching. Cano- Marquez et al.,3 on the other hand, obtained GNR by treating multiwalled carbon nanotubes with lithium and ammonia. Oxidative cutting was used by Liu et al.4 to transversally cut long nanotubes into smaller tubes and Li et al.5 provided insight into the atomic-level mechanisms of oxidation in carbon . Due unavailability of argon gas & plasma etching system I will not follow this method. [10]

2. ***"Intercalated method"*** is used to separate each graphene plane from 3D graphite. Here graphene planes became separated by layers of intervening atoms or molecules. The major disadvantages of this method is; large molecules could be inserted between atomic planes, providing greater separation, resulting compounds having isolated graphene layers embedded in a 3D matrix. [11]

3. There has been report of preparation of regular size graphene sheet through ***"chemical method"*** to unzip MWCNT. It's the most economy & efficient way. So I will follow the chemical method discussed by et al.; Nature paper; Vol. 458 16 April 2009; doi:10.1038/nature07872 [12].

CHAPTER 2

PROCEDURE

2.1 Steps followed for Unzipping via chemical method:

A) Pre-oxidation

B) Oxidation

2.1.1 Pre-oxidation

In pre-oxidation method the MWCNT was treated with concentrated sulphuric acid (H_2SO_4) and Nitric acid (HNO_3) to enhance oxygen. MWCNT was suspended in a mixture of 50 ml of H_2SO_4 and 25 ml of HNO_3 for more than 12 hours. 50 ml of H_2O was added to accelerate the reaction. Next day stirring was done for 10 min. After 24 hours MWCNT was collected in the bottom of beaker and washed with H_2O for several times to remove acids. By help of a ph paper acidic nature was tested. Then solution was dried to collect CNT power.

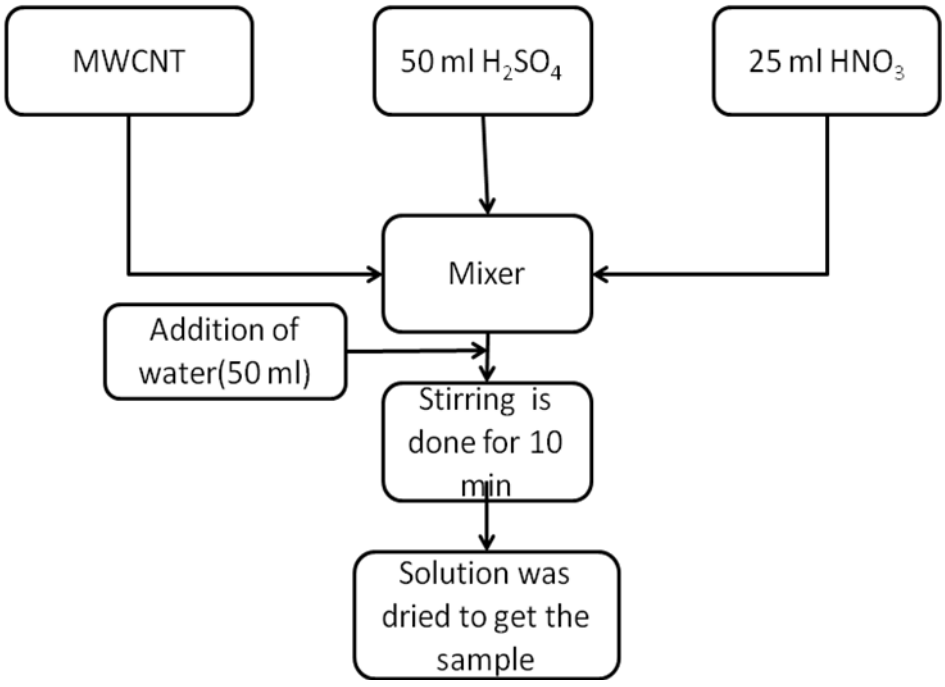

Fig 2.1 PREOXYDATION FLOW CHART

2.1.2 Oxidation

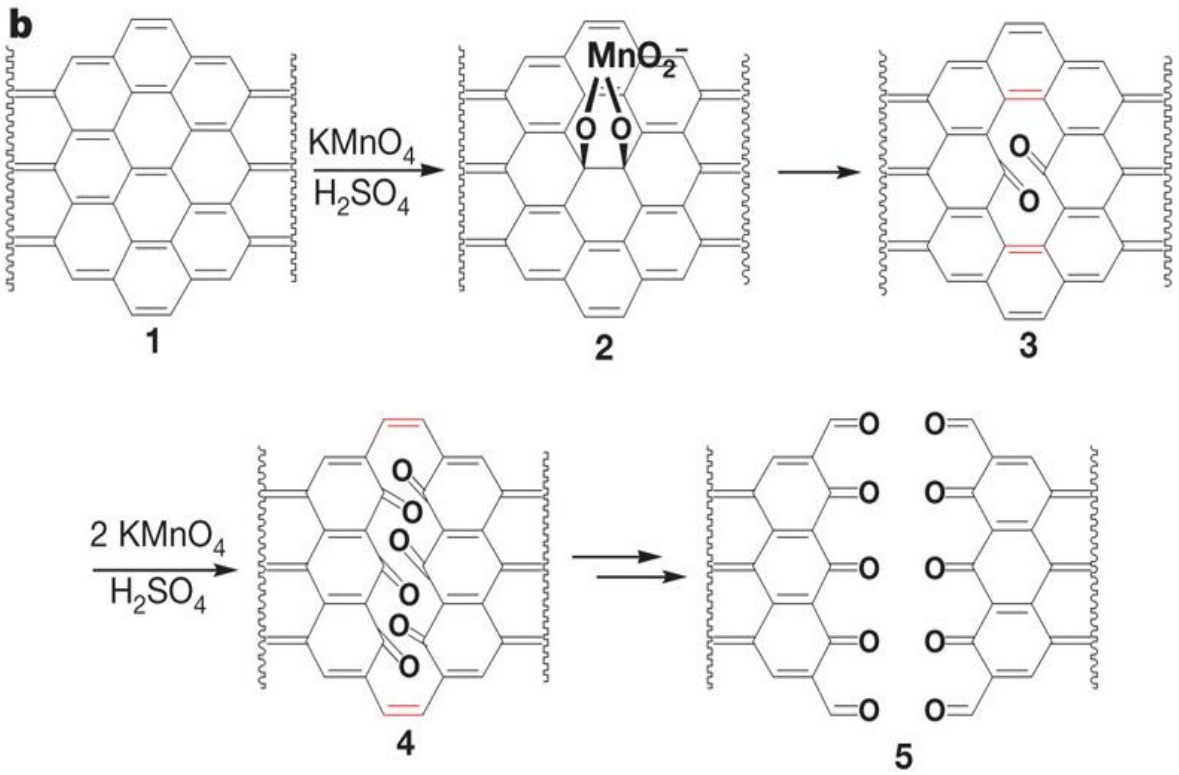

Fig 2.1 – Representation of the gradual unzipping of one wall of CNT.

MWCNT will be suspended in concentrated 50 ml of sulphuric acid (H_2SO_4) for a period of 1–12 h. Then solution was treated with 500 wt% potassium permanganate ($KMnO_4$). The H_2SO_4 conditions aid in exfoliating the nanotube and the subsequent graphene structures. The reaction mixture was stirred at room temperature for 1 h and then heat for 50–70^{0}C for an additional 1 h. Now quenches the reaction mixture by pouring over ice containing a small amount of hydrogen peroxide (H_2O_2). The solution was filter over a poly tetra fluoro-ethylene (PTFE) membrane, and the remaining solid to wash with de-ionized water. Then dried CNT was collected. [12]

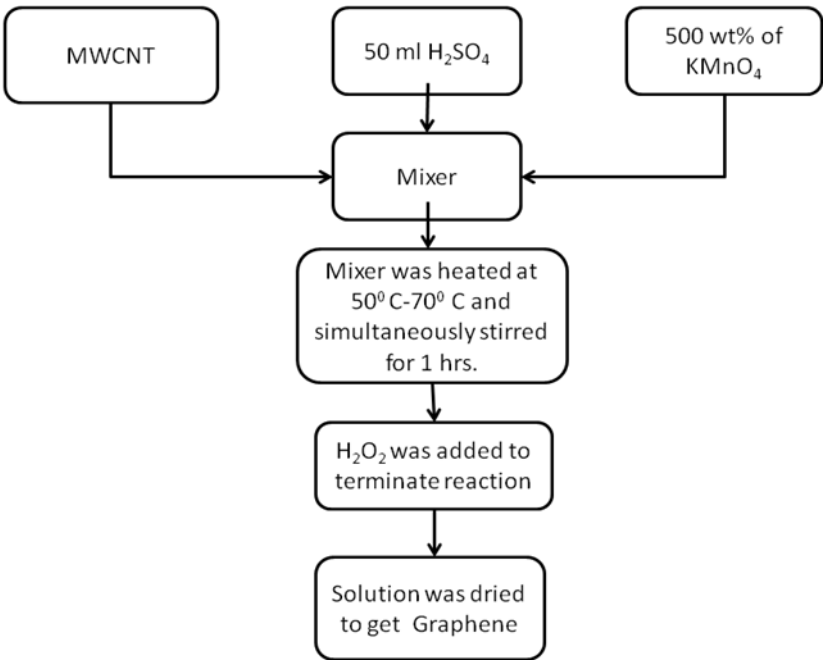

Fig 2.1 OXIDATION FLOW CHART

2.2 Formation of manganate ester or attacks of $KMnO_4$

(5,5)CNT, MnO_4 Structures (fig 2.3)	*Energy (hartree)*	*Binding energy (kcal/mol)*	*C–C distance (Å)*
CNT	-3808.165,69		
$MnO4^{-1}$	-1451.669,16		
MnO4-^{1} on b1	-5259.87561	-25.6	1.62
$MnO4^{-1}$ on b2	-5259.87013	-22.1	1.62
$MnO4^{-1}$ on b3	-5259.85924	-15.3	1.62
$MnO4^{-1}$ on b4	-5259.86786	-20.7	1.71
$MnO4^{-1}$ on b5	-5260.08458	-156.7	1.42
Nonbonded	-5259.85624	-13.4	1.22

Table 2.2 Energies and binding energies for the CNT [9]

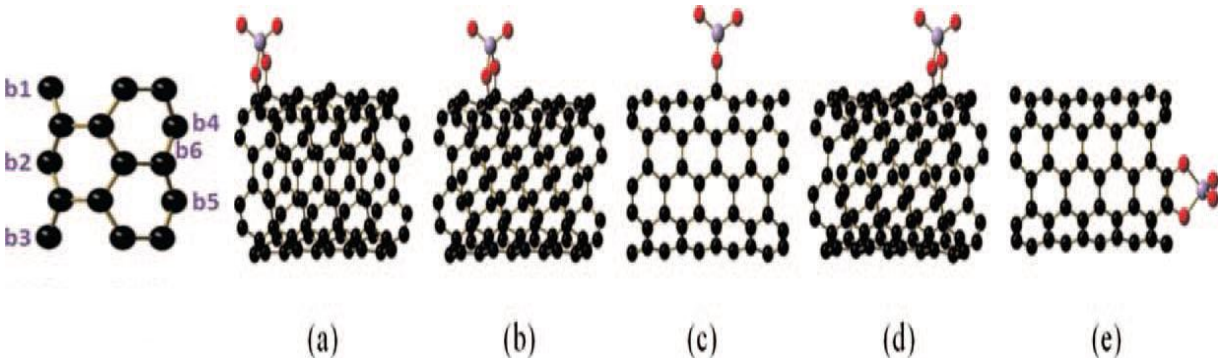

Fig 2.3 - Optimized geometries ((a)–(e)) of the structures obtained when approaching the opener anion MnO_4^{-1} to the CNT connecting initially two of the oxygen atoms from the permanganate to the b1–b5 bonds, respectively.

The total binding energies, are shown in Table 2.2 for the (5, 5) CNT, the permanganate anion (MnO_4^{-1}), and the anion bonded to the b1–b5 bonds along with the unbounded $MnO4^{-1}$ interacting in the neighborhood of the (5, 5) CNT. Also shown in Table 2.2 is the distance of the carbon atoms participating in the ester formation.

The energies shown in Table 2.2 suggest that MnO_4^{-1}, the anion, attacks the CNTs bonds because the energy of the overall system for the bound anion (onto b1–b5) is lower than the energy for the unbound one. The binding energy of the unbound one, (13.4 kcal/mol, is 2 kcal/mol higher than the weakest binding energy of a bound anion to the CNT (onto b3), (15.3 kcal/mol. Even though the lowest total energy (singlet multiplicity) is attained when the permanganate anion binds to the edge bond B5, the attack leaves the bond unbroken, the C-C distance in b5 goes from 1.24Å to 1.42 Å. Whereas when the anion binds to the CNT on b1–b4, the C–C distance in the bonds increases 0.2 Å to 0.3 Å, leading to their rupture and thus to the partial unzipping of the nanotube.

CHAPTER 3

CHARACTERIZATION AND RESULT DISSCUTION

3.1 Characterization Techniques

The following characterization techniques were used to study the structural, morphological properties of CNT.

3.1.1 X-ray diffraction (XRD)

The physical properties of CNTs greatly depend on how sheets have been rolled up, the tube and length diameter, aspect ratio (ratio between diameter and length of CNT) and the nanotube morphology. X-ray methods offer structural information at different length scales from the single nanotube to the nanotube bundle. Semi-crystalline polymers, composites and in particular SWCNT polymer nanocomposites are hierarchically organized materials. The understanding of the macroscopic properties in terms of microscopic models requires an analysis of the characteristic order appearing at different length scales.

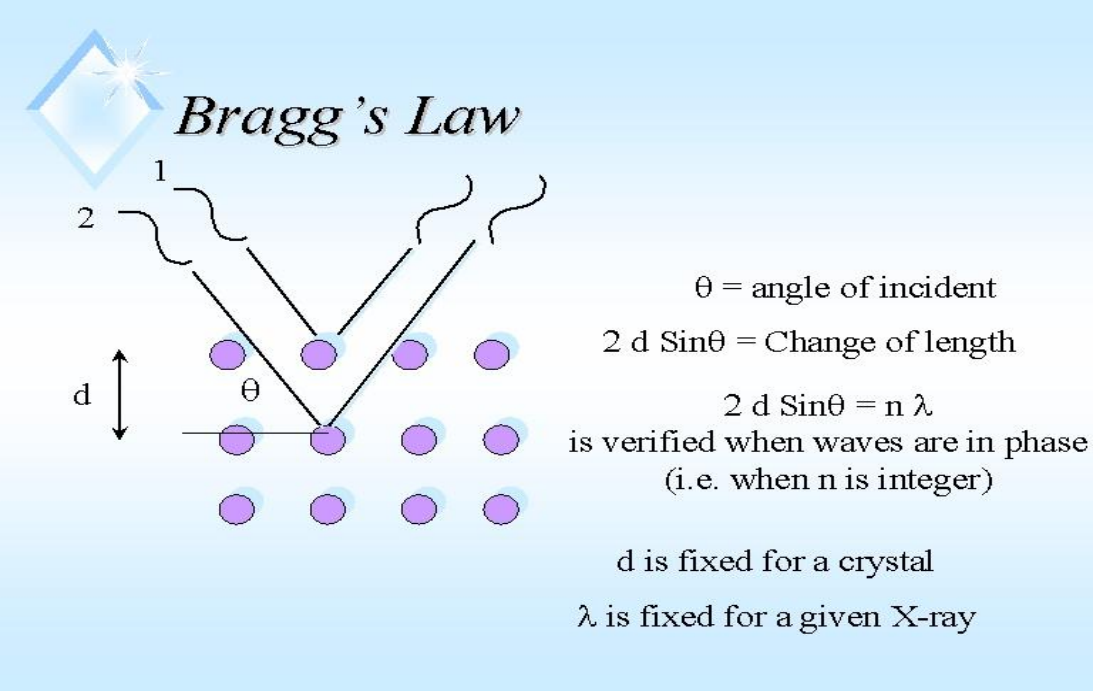

Fig. 3.1 – X-Ray phenomena

X Rays are electromagnetic radiation, used for phase identification of a crystalline material & can provide information on a unit cell dimension. XRD is based on constructive interference of the monochromatic x-ray & crystalline sample when the condition satisfies Bragg's law. ($n\lambda = 2d \sin\theta$)

The diffracted x-rays are then detected, processed & counted. By scanning the sample through a range of 2θ angle all possible diffraction direction of the lattice should be attained due to random orientation of powder crystal. Conversion of diffraction peak to d-spacing allows identification of a mineral because mineral has a set of unique d – spacing.

3.1.2 Scanning electron microscope (SEM)

A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a beam of electron in a raster scan pattern .In SEM, a beam of highly energetic electrons strike the sample. The secondary electron, back scattered, are ejected from the sample. The electron interacts with the atoms that make up the sample producing signals that are collected at the detector. This signal contains information about the samples surface, composition, topography and electrical conductivity.

Fig 3.2 – JEOL SEM Machine

3.1.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) compatible chips have received increased attentions, as TEM allows detailed study of the structure of nanodevices.

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of visible light. A light source at the top of the microscope emits the electrons to travel through vacuum in the column of the microscope. Instead of using glass lenses to focus the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into very thin beam. These electron beams then travels through the sample. Depending on the density of the sample, some of the electrons are scattered or disappear from the beam. At the bottom position of microscope the unscattered electrons hit a fluorescent screen, which gives rise to a shadow image of the specimen with its different parts displayed in varied darkness according to their density. The image then studied directly by the operator or photographed with a camera.

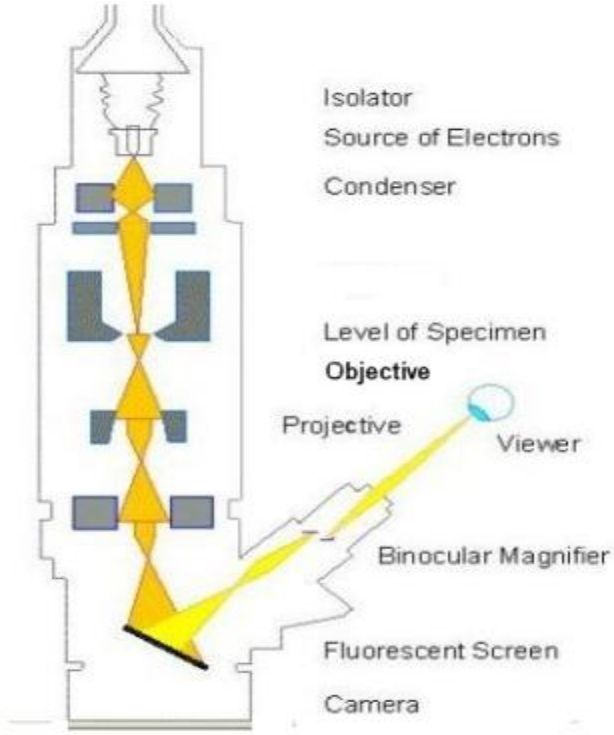

Fig 3.3 - TEM Microscope ray diagram

3.2 XRD study

The crystal phases and structure information of the CNT products were obtained by XRD plotting. Due to the fact that in an isolated SWCNT only one graphitic layer is involved X-ray diffraction is absent because, the diffraction condition requires the existence of several planes repeating periodically in real space.

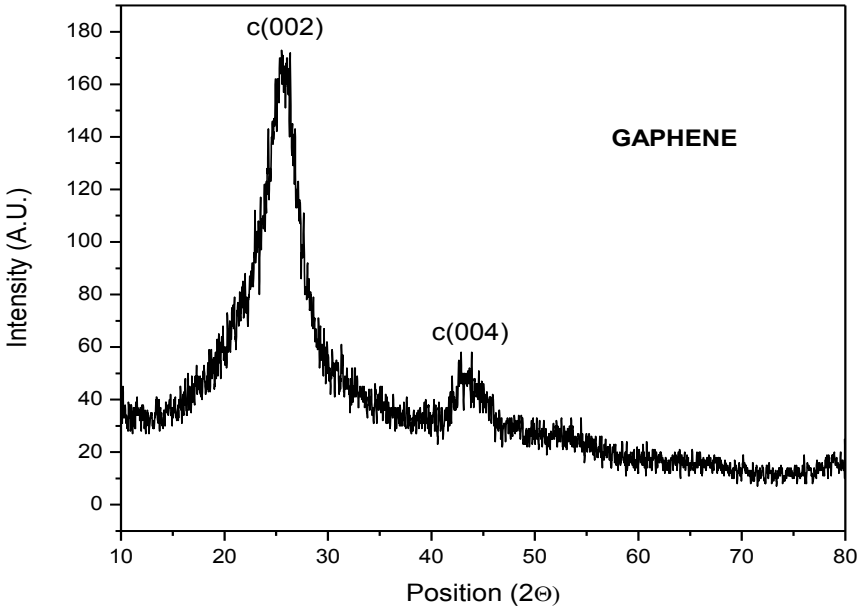

Fig – 3.4 XRD patterns of graphene samples showing graphite peaks G (002) & G (004)

From XRD plot we can see the wide peak, which is due to the splitting of the CNT (tube) into several graphene nanoribbons (GNR), resulting in the decrease of the crystalline domain.

By doing analysis of x-ray diffraction pattern of Graphene, we got high intensity peaks of carbon. The first peak is f C(002) at angle (2θ) 26.4^0 having Interlayer spacing (d) is 0.337 nm.

shearer formula,

$$D = 0.9\,\lambda/(B\cos\theta)$$

Where, D= Average particle size

λ = wave length of XRD ($1.54A^0$)

B= Full wave half maxima

Average particle size was calculated from *shearer formula* and found to be 1.79 nm. Both values of interlayer spacing (d) and average particle size (D) is comparable with previously calculated data.

3.3 SEM Image

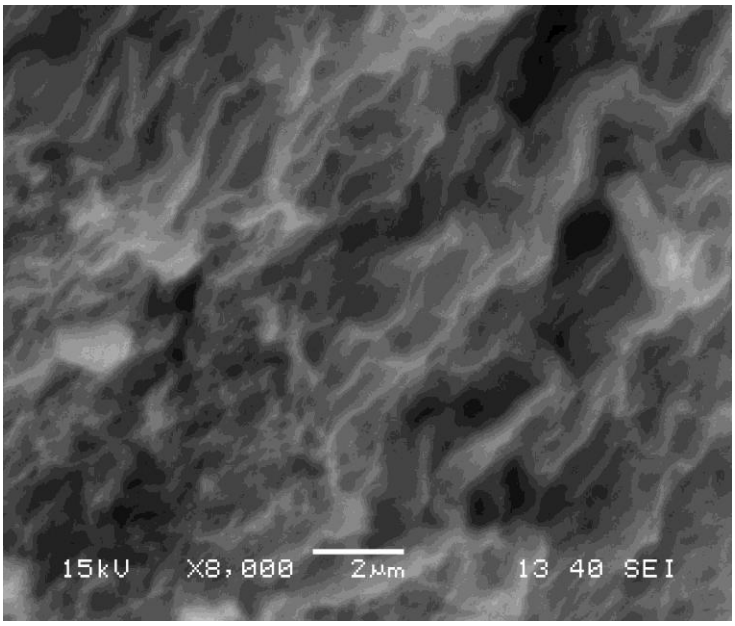

Fig – 3.5 SEM image of MWCNT

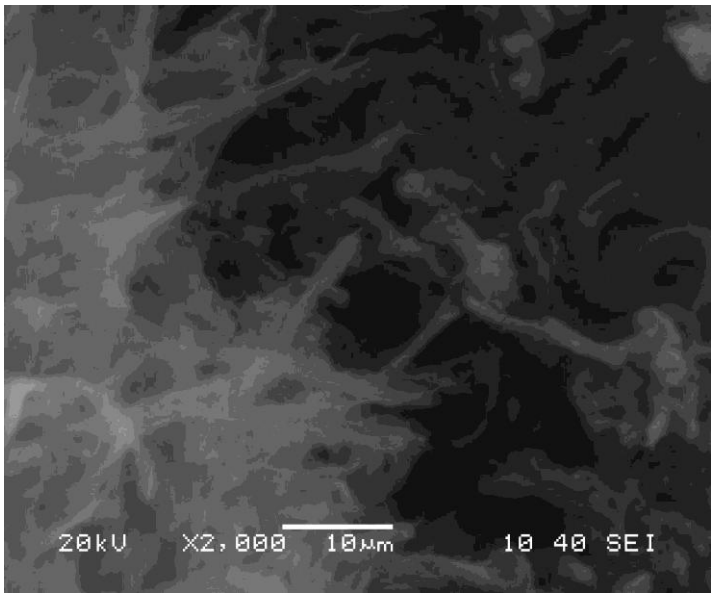

Fig – 3.6 SEM image of MWCNT

Carbon nanotubes (CNT) were revealed under electron microscope in figure 3.5 and 3.6. at different frame size.

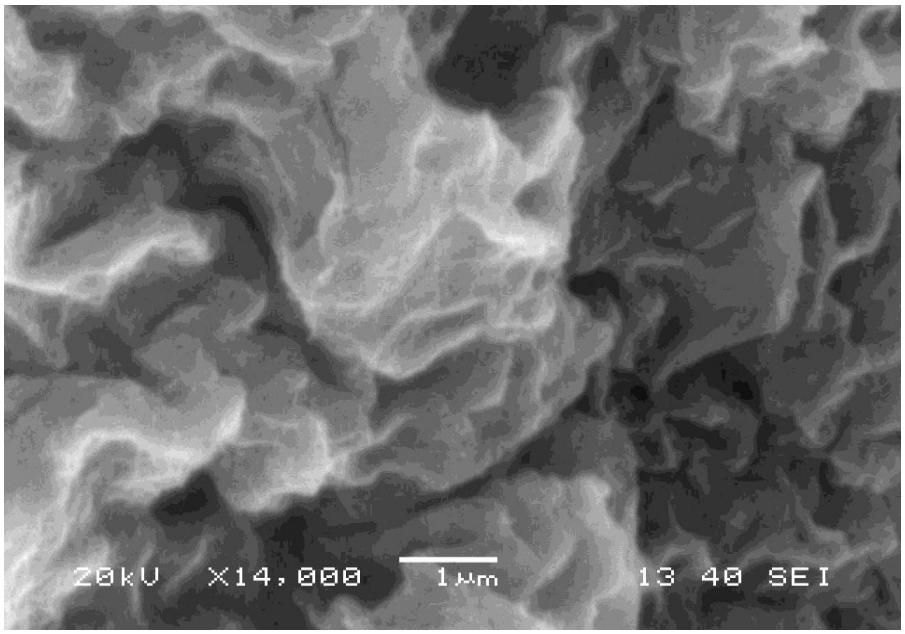

Fig – 3.7 SEM image of MWCNT after unzip

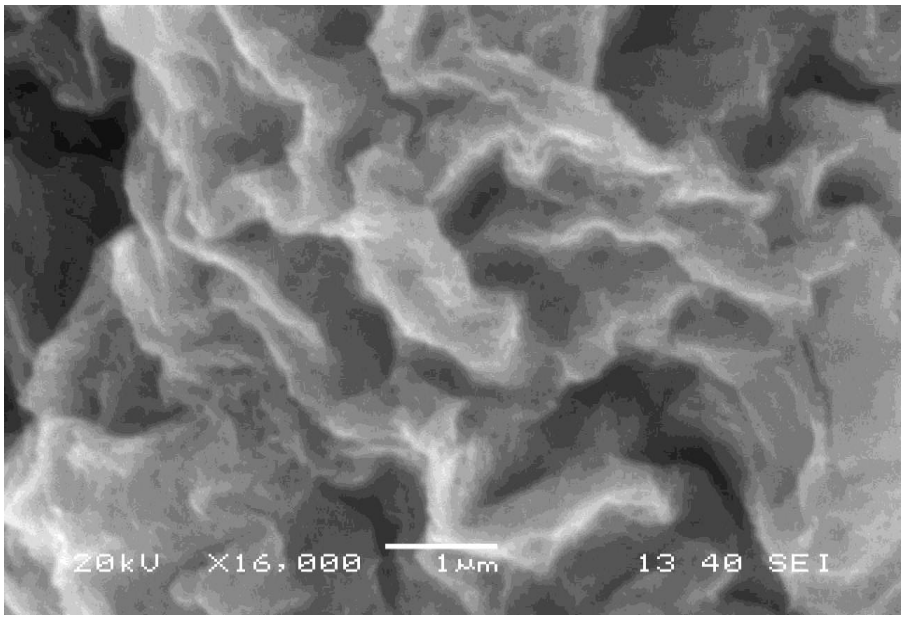

Fig – 3.8 SEM image of MWCNT after unzip

Fig. 3.7 and 3.8 shows some of the SEM images corresponding to nanotubes after being unzipped.

3.4 TEM

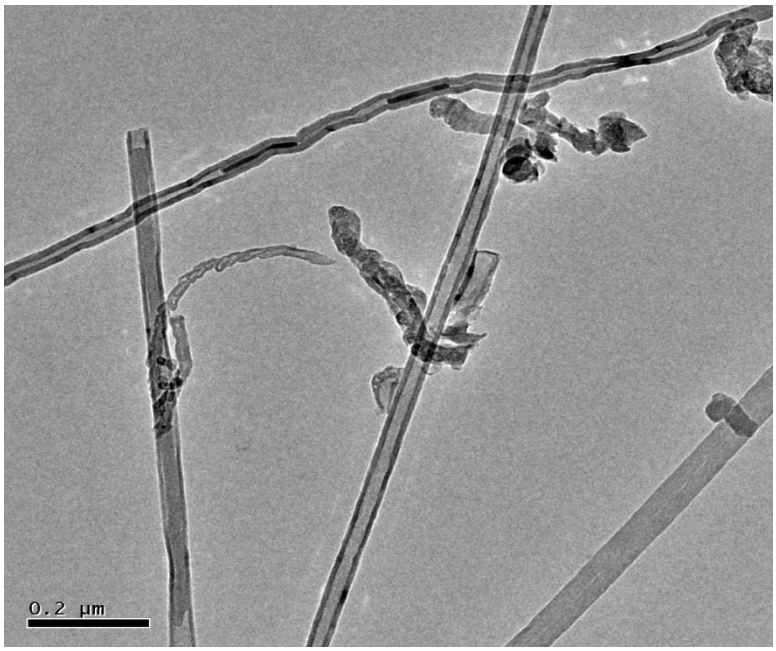

Fig. 2.8 TEM micrographs CNT sample

The microstructure of the aligned CNTs was investigated using TEM in Fig 2.8. It confirms the well crystallized multi-layered graphitic tubular structure. The black spots in Fig 2.8 are attributed to impurities like K, Mn metals and amorphous carbon on the surface and inside the core of the nanotubes. The images show that the average diameter of the CNTs is in the range of 30 - 50 nm.

CHAPTER - 4

CONCLUSION

Unzipping of MWCNT was carried out via chemical method by the help of sulphuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$). This is the economical and efficient way to get graphene ribbons from CNT.

XRD analysis usually involves the identification of a phase in sample. By analyzing the data from x-ray diffraction, we found that the Interlayer spacing (d_{002}) is 0.337 Ao and the average particle size is calculated by using shearer formula and is found to be 1.79 nm. Both the values of the interlayer spacing (d) and the average particle size (D) is comparable with previously mentioned data [15,16]. So graphene formation is confirmed. Unzipping of MWCNT was confirmed also from SEM images. TEM image shows impurity metal and amorphous carbon are present in spaceman.

CHAPTER 5

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